1708

THE ACTION OF HEAT AND MOISTURE ON LEATHER

PART I. THE STORAGE OF A VARIETY OF COMMERCIAL LEATHERS AT 40°C. AND 100% R.H.*

J. H. BOWES AND A. S. RAISTRICK

British Leather Manufacturers' Research Association
Milton Park, Egham, Surrey, England

ABSTRACT

Studies of the deterioration of leather under warm moist conditions have mainly been concerned with heavy upper leathers of high grease content. In the present work a survey of the behavior of a selection of commercial leathers of various types has been made in order to form a general background to a program of research on the mechanism of the deterioration of leather.

The leathers were stored over water at 40°C. for 6 months, and losses in strength and changes in crackiness, shrinkage temperature, and pH of water extract were determined.

Chrome leathers were the most resistant to the action of heat and moisture and, with the exception of the one sole leather tested, lost little or no strength. Some of the vegetable-tanned leathers also lost relatively little strength but darkened in color and tended to become rather cracky. The resistance of the majority of the semi-chrome and chrome retan leathers was poor, and losses of strength of 80% occurred in some cases. The shrinkage temperature of most of these leathers fell by 10° or more during storage.

The possible causes of the low resistance of these leathers are considered, and their bearing on the behavior of these leathers in wear are discussed.

Limited tests on the same leathers stored over water at 20°C. or in air at 40°C. indicate that little deterioration occurs under these conditions, emphasizing that it is the combined action of heat and moisture which is deleterious.

INTRODUCTION

The damage to leather which may be caused by the combined action of heat and moisture has long been recognized. The extent to which such

*The work reported in this paper forms part of a Research Program sponsored by the U. S. Department of Agriculture under the authority of U. S. Public Law 480.

damage may occur as the result of prolonged exposure to high humidities but relatively low temperatures, however, does not seem to have been fully realized until wartime conditions necessitated the prolonged storage of army footwear under tropical conditions. Work in the last ten to fifteen years has shown that storage under moist conditions at 30°C. or above causes appreciable losses in strength of chrome, vegetable, semichrome, chrome retan, and other combination-tanned leathers (1–10). Increased stiffness, crackiness (2, 9), and fall in shrinkage temperature (5, 7) are also reported. Although mold growth usually occurs when the temperature of storage is 40°–50°C., there is little evidence that this influences the strength or other properties except in so far as it affects the grease (2–6). In some investigations a fall in the pH of water extract of vegetable and retan leathers is reported (4, 5, 11).

Much of this work (4, 5, 7, 9) has been carried out on leathers of high grease content, over 20% in most cases. Changes in the grease have been shown to result in losses of strength (2, 3, 12), and it is, therefore, not certain how far losses in strength are due to such changes in the leather fibers themselves. Also, in the main it has been concerned with heavy-weight vegetable, chrome, semichrome, and more particularly chrome retan leathers prepared for the U.S. Army. Little information on commercial leathers of lower grease contents, other than chrome retan (10, 11), appears to be available. A broad survey of the behavior of a selection of typical commercial sole, insole, upper, and gloving leathers has, therefore, been undertaken in order to form a background to a general research program on the mechanism of the deterioration of leather. In Part II a more detailed examination of the progress of deterioration of vegetable, chrome, semichrome, and chrome retan leathers is described.

EXPERIMENTAL

Notes on leathers examined.—Thirty leathers of various types were collected as indicated in Table I. The leathers classified as semichrome were vegetable-tanned (O, P, and Q, in India) and were retanned with chrome. Those classified as chrome retan, were chrome-tanned first and then given varying degrees of vegetable retannage.

The vegetable-tanned sole leather samples B1–B4 were cut from the same bend and had been treated to reduce water solubles. B1 was untreated; B2, treated with 1% formaldehyde on leather weight; B3, with 1% formaldehyde and 1% urea; and B4, with 0.7% dimethylol urea.

The two vegetable-tanned insoles were from similar tannages consisting of a catechol-pyrogallol blend. The semichrome and chrome retan insoles were from the same firm as the vegetable-tanned insoles, had received a similar vegetable tannage, and were of the same substance. The chrome sole samples F and G were from the same bend before (fore end) and after (tail end) waxing.

TABLE I

ANALYSIS OF LEATHERS

Description of Leathers	Insoluble Ash	Grease	Water Solubles	Fixed Tan	Degree of Tannage	Cr_2O_3 *% moisture and grease free*
	(*% moisture free weight*)					
Vegetable						
A Sole	0.46	5.2	21.1	33.2	82.8	—
B1 Sole	0.64	4.5	23.1	32.5	82.9	—
B2 Sole, formaldehyde-treated	0.58	5.1	6.0	45.6	107	—
B3 Sole, treated with formaldehyde plus urea	0.45	5.1	2.9	44.9	96.1	—
B4 Sole, treated with dimethylol urea	0.37	4.6	2.9	39.9	76.4	—
C Insole, shoulder	0.48	9.2	21.4	29.0	72.7	—
D Insole, butt flesh split	0.26	3.8	8.3	28.3	47.6	—
E Upholstery	0.19	2.5	12.5	33.4	65.0	—
Full Chrome						
F Sole, before waxing	—	1.3	—	—	—	6.89
G Sole, after waxing	—	32.4	—	—	—	6.68
H Side, dyed	—	5.1	—	—	—	5.99
I Side, dyed	—	1.7	—	—	—	5.41
J Side, dyed	—	4.4	—	—	—	4.33
K Side, dyed	—	3.5	—	—	—	4.01
L Calf upper, dyed	—	4.0	—	—	—	6.04
M Cape gloving, dyed	—	6.2	—	—	—	2.85
N Cape gloving	—	10.0	—	—	—	3.26
Semichrome						
O E.I. kip, crust	0.63	8.4	2.6	31.8	57.9	0.76
P E.I. kip, dyed	0.69	9.4	1.5	33.8	66.0	1.52
Q E.I. kip, dyed	1.21	5.3	1.2	27.5	49.2	2.74
R English side	0.66	11.3	0.3	29.3	51.3	1.66
S Insole, shoulder	0.38	8.2	9.9	33.8	74.9	1.12
T Insole, butt flesh split	0.59	5.5	2.4	32.2	56.2	0.74
Chrome Retan						
U Sole	0.82	4.7	23.1	28.4	69.1	0.78
V Side	0.82	5.0	1.1	7.1	9.7	5.44
W Insole, shoulder	0.74	6.4	4.9	33.0	58.3	2.81
X Cape gloving	7.30	10.4	3.7	9.7	15.3	2.61
Miscellaneous						
α Zirconium, hide, grain split	—	—	—	—	—	—
β Chamois	—	—	—	—	—	—
γ Chamois, rot-resistant	—	—	—	—	—	—

The two gloving leathers N and X were from the same tannage, but X had been given a further treatment with 25% liquid vegetable tanning extract based on mimosa and 2–3% syntan on dry weight. M had been lightly dyed with neolan and wood dye.

Of the two chamois leathers, γ had been classified as rot-resistant by a rapid incubation test (13). Neither contained any detectable formaldehyde.

Sampling and storage.—Samples were cut from the britch areas of most leathers (A, D, G–L, O, P, R, T, U, and V), from the fore end of the butt of F, and from the center of the half shoulders, D, S, and W, about 4″ from the backbone. With the small skins, samples were taken from each side, avoiding the backbone. The location of samples E, Q, and α was not known.

For the examination of the effect of storage over water at 40°C. samples were all cut from an area 12″ x 8″ in such a way that each test sample could be paired with a corresponding control sample adjacent to it, so that the actual tests on control and deteriorated leathers were made as near to each other as possible.

The test samples were suspended over water in glass tanks 5″ x 7″ covered with a glass plate and stored in an incubator at 40°C. for 6 months. A small beaker containing toluene was placed in each tank to discourage mold growth. The corresponding control samples were stored in polyethylene bags in the laboratory at temperature 18°–22°C. Both sets of samples were then tested together, and the percentage loss in strength for each pair was calculated.

Further samples of some of the leathers were stored for 6 months over water at 20°C. or hanging freely in an incubator at 40°C. In this case only six samples 6″ x 1½″ for buckle tear tests were included, measurements being made on the same samples before and after storage.

After removal from the tanks the leathers were air-dried.

Examination of leathers.

Analyses.—The analysis of the original leathers was carried out by the official S.L.T.C. methods (14). Chrome was determined by perchloric acid oxidation. Fixed tan in the combination-tanned leathers was calculated by difference using a factor of 2.5 × Cr_2O_3 for "chrome tan". For pH of water extract 2.5 g. leather, either ground or in small pieces 2 mm. sq., were extracted with 50 ml. water for 24 hours at room temperature with occasional shaking (A.L.C.A. Official Method D35). The analyses are recorded in Table I.

Physical tests.—The leathers were conditioned at 21°C. and 70% R.H. Buckle tear loads on samples 4″ x 1.5″ and tensile strength (breaking load) were determined as described in S.L.T.C. Official Methods (14). Percentage losses in strength for each pair of samples were calculated. With most leathers there was reasonable agreement between replicates, but only differences of ten or more in the figures for percentage loss can be considered real.

RESULTS

In spite of the presence of toluene mold, developed on some of the leathers stored over water at 40°C.; on the vegetable-tanned leathers B1, B2, B3,

TABLE II

SOME EFFECTS OF MOIST STORAGE AT 40°C.

Leather and Tannage	Water Uptake during Storage	Mold Growth*	Crackiness after Storage*	pH of Water Extract		Shrinkage Temperature °C.	
				Control	Stored	Control	Stored
Vegetable							
A	13	++	++	3.61	3.48	77	81
B1	29	++++	+	3.68	3.49	78	87
B2	15	++++	++	3.48	3.18	93	96
B3	21	++++	++	3.46	4.16	96	98
B4	32	++++	+++	3.50	5.43	94	98
C	11	++++	+	3.58	3.19	74	82
D	23	0	+	4.43	4.10	77	84
E	34	++++	+	3.44	3.34	71	82
'ull Chrome							
F	38	0	++	3.65	3.46	112	114
G	31	0	++	3.57	3.52	110	114
H	28	0	0	3.52	3.32	115	117
I	35	0	0	3.08	2.95	110	115
J	39	0	0	3.03	2.96	101	109
K	45	+	0	3.24	3.24	112	114
L	22	0	0	3.68	3.95	110	115
M	170‡	+	0	4.35	4.48	98	100
N	77‡	0	0	4.85	4.74	102	104
Semichrome							
O	19	+	++	2.98	3.09	89	78
P	21	0	+	3.35	3.28	99	76
Q	36	++	+	3.52	2.99	119†	97†
R	25	0	+++	3.14	3.03	98	83
S	40	0	+++	2.68	2.68	78	77
T	19	++	+	3.08	2.84	89	73
Chrome Retan							
U	22	++	++	3.73	3.35	81	86
V	32	0	+	3.28	3.24	114†	112†
W	18	0	++	3.15	2.93	112†	100†
X	41	++	0	4.46	4.15	99	96
Miscellaneous							
α	57	++	—	3.84	3.56	84	85
β	151‡	0	—	—	—	64	63
γ	44	0	—	—	—	73	71

* +very slight; ++ slight; +++ medium; ++++ extensive
† Shrinkage temperatures of all chrome leathers and those indicated by †, determined in 75% glycerol/water.
‡ Leather stretched during storage and may have touched water surface.

B4, C, and E and on the retan leather U after one month, and on a number of others at a later stage. The extent of this mold growth at the end of the six-month storage is indicated in Table II.

The uptake of water during storage was determined, as it was thought that this might influence deterioration. No correlation with loss of strength or other changes could be detected, however.

TABLE III

THE EFFECT OF STORAGE OVER WATER AT 40°C. ON STRENGTH

Leather and Tannage	Buckle Tear Load		Tensile Strength Breaking Load	
	Control lb.	% Strength Retained after Storage	Control lb.	% Strength Retained after Storage
Vegetable				
A	487	51	455	50
B1	408	89	476	70
B2	260	87	356	71
B3	291	83	335	57
B4	317	89	277	77
C	150	91	270	66
D	162	80	355	65
E	69	85	225	44
Full Chrome				
F	318	46	315	67
G	319	49	432	63
H	56	108	97	105
I	93	117	233	105
J	59	100	137	77
K	52	116	106	100
L	12	102	42	110
M	58	83	—	—
N	13	114	—	—
Semichrome				
O	59	53	157	46
P	81	56	230	54
Q	41	52	106	35
R	43	35	92	28
S	191	32	276	17
T	92	31	151	35
Chrome Retan				
U	391	66	437	59
V	66	83	104	64
W	42	23	68	21
X	11	60	—	—
Miscellaneous				
α	31	93	95	87
β	11	19	—	—
γ	8	87	—	—

The chrome leathers were the least affected by the warm moist storage. There was little change in their appearance, and with the exception of the sole leather, they lost little or no strength. (*See Table III.*) The leathers tended to become rather stiffer, but only the sole leather, both waxed and unwaxed, showed signs of crackiness. Contrary to the observations of some workers (7) the shrinkage temperature of most of the chrome leathers increased by 2°–10°C. (*See Table II*).

The vegetable-tanned leathers darkened in color and all developed some degree of crackiness, but with the exception of leather A, losses in buckle tear load were less than 20%. Losses in tensile strength were rather greater but still relatively small compared with that of most of the vegetable-chrome combination leathers. After determination of the shrinkage temperature the leather samples were somewhat gelatinous in appearance and texture, suggesting that there had been some loss of cohesion during the storage which,

TABLE IV

THE EFFECT OF STORAGE OVER WATER AT 20°C. OR IN AIR AT 40°C.

Leather and Tannage	% Strength (Buckle Tear Load) Retained after Storage		Shrinkage Temperature °C.	
	20°C. over water	40°C. in air	20°C. over water	40°C. in air
Vegetable				
A	101	108	74	74
C	106	103	73	73
E	104	105	68	67
Chrome				
F	106	101	114	109
G	120	89	110	107
H	106	107	116	109
I	126	100	111	105
J	120	107	105	88
L	125	113	109	98
N	99	102	95	90
Semichrome				
O	89	95	85	82
P	97	97	95	92
R	98	78	91	88
T	99	95	85	84
Chrome Retan				
U	99	95	84	80
V	98	84	111	105
W	90	84	103	102
X	90	90	90	91
Miscellaneous				
α	110	98	84	63
β	102	83	64	59
γ	110	—	70	—

on heating, allows some disorganization of the collagen structure. The apparent increase in shrinkage temperature on storage is probably due to this, stretching of the sample masking the initial stages of the fiber shrinkage.

The resistance of the semichrome and retan leathers was almost uniformly poor; they became darker in color, the strength of many was reduced by 50% or more, and a few became very cracky on the grain, e.g., R and S. The only leathers which retained a reasonable proportion of their strength were the lightly retanned side of high chrome content (V) and to a lesser extent the sole leather which contained little chrome and was not very different from a vegetable-tanned leather.

Of the miscellaneous leather, the zirconium behaved similarly to the chrome-tanned upper leathers. The oiled, tanned leather γ, classified as rot-resistant, was almost unaffected by storage, but the other was harsh in appearance and feel and became very weak. The greater resistance of leather γ is probably associated with its higher shrinkage temperature, indicating that cross links may have been formed from aldehydes produced by oxidation of the oil.

The limited tests carried out on the effect of storage over water at 20°C. or in the air at 40°C. indicate that under these conditions there is little loss of strength or general deterioration. (*See Table IV.*)

Apart from some darkening of the leathers containing vegetable tan, moist storage at 20°C. had no obvious adverse effects, and the strength of the vegetable and chrome leathers was, in fact, slightly increased. Dry storage at 40°C. also caused small increases in the strength of the vegetable and chrome leathers, but there were slight decreases with the semichrome and chrome retan leathers. The strength of the waxed chrome sole also decreased, probably because of changes in the grease. This leather, and also the unwaxed chrome sole, became cracky, and the vegetable and retan soles rather cracky, but the other leathers were apparently unaffected.

The shrinkage temperature of the combination-tanned leathers was decreased by 5°–10°C. by storage under both conditions, and that of the chrome and zirconium leathers by about 10°C. by dry storage at 40°C. The shrinkage temperature of the other leathers was unaffected.

DISCUSSION

It is clear from these results that it is the combined action of heat and moisture which is deleterious to leather rather than either heat or moisture alone, and that the type of tannage, vegetable, chrome, or combination of vegetable and chrome, is one of the most important factors governing stability. It may be deduced that chrome leather is likely to be the most resistant, and that vegetable-tanned leathers of relatively good resistance can also be produced, but that semichrome leathers, as well as chrome retan leathers, are likely to deteriorate badly under such conditions.

The stability of the majority of chrome-tanned leathers tested does not ubstantiate earlier work (5, 7, 9), in which appreciable losses in strength were found under comparable conditions. In most cases, however, these losses in strength were observed with leathers of high grease content, or with sole or heavy army upper leathers similar to the chrome sole in the present investigation. The poorer resistance of such heavy-substance leathers remains unexplained; in the present work it was not associated with any difference in pH or in chrome content or distribution.

Variations in stability of any one type of leather could not be directly related either to pH or to the composition of the leather. The relatively high stability of the lightly retanned leather V is probably due to its high chrome content, and the loss of strength of the chrome gloving M may be associated with the use of a vegetable mordant.

The poor stability of chrome retan leathers has been observed by Sykes and Williams-Wynn (10, 11, 15), both under normal and accelerated conditions of aging. As in the present investigation they found a fall in pH of water extract, which was later followed by an increase which they attributed to hydrolytic breakdown of the collagen. It is generally agreed that during retannage with vegetable tans sulfate or other anions are displaced from the chrome complex, and Amos, Thompson, and Tolliday (17) have shown that this displacement continues when the leather is stored wet. As suggested by Sykes and Williams-Wynn (10) such displacement probably accounts for the fall in pH of chrome retan leathers on storage, Chrome is also displaced during retannage (17), and it seems likely that carboxyl groups of the protein are also slowly displaced from the chrome complex during storage, leading to detannage. Such a mechanism would account for the large falls in shrinkage temperature which occurred during storage.

Although the semichrome and retan leathers are more affected by moist heat than chrome- or vegetable-tanned leathers, it does not necessarily follow that this will also be true in wear. Experiments have shown that the presence of vegetable tannins reduces the amounts of chrome which can be extracted from leathers by lactate solutions (18); hence such leathers may be more resistant to the detanning action of perspiration than full chrome leathers. Also, since perspiration tends to increase the pH of the leather, thus increasing oxidation of tan and displacement of chrome (19), the slow production of acidity by the combination-tanned leather may be beneficial rather than deleterious in wear.

REFERENCES

1. Kanagy, J. R., and Tobias, P. E. *JALCA*, **37**, 426 (1942).
2. ———, Charles, A. M., Abrams, E., and Tener, R. F. *JALCA*, **41**, 198 (1946).
3. ———, Seebold, R. E., Charles, A. M., and Cassel, J. M. *JALCA*, **44**, 270 (1949).
4. Lollar, R. M. *JALCA*, **49**, 605 (1954).

5. Roddy, W. T., and Jansing, J. J. *JALCA*, **49**, 773 (1954).
6. Mitton, R. G., and Turner, J. M. *J. Soc. Leather Trades Chemists*, **39**, 343 (1955).
7. Mann, G. W., and Steiner, E. T., as quoted by Seligsberger, L., and Mann, G. W., in *Chemistry and Technology of Leather Manufacture*, Vol. II (New York: Rheinhold, 1958) 489.
8. Seligsberger, L., Mann, G. W., and Clayton, H. *JALCA*, **53**, 627 (1958).
9. Mitton, R. G., and Wyatt, K. E. Unpublished.
10. Sykes, R. L., and Williams-Wynn, D. A. *J. Soc. Leather Trades Chemists*, **45**, 214 (1961).
11. ——— — ———. *Ibid.*, **43**, 265 (1959).
12. Mitton, R. G. Unpublished.
13. Green, G. H. Unpublished.
14. Official Methods of Analysis. *Soc. Leather Trades Chemists.* 1957.
15. Sykes, R. L. and Williams-Wynn, D. A. *J. Soc. Leather Trades Chemists*, **45**, 16 (1961).
16. Amos, G. L., Thompson, G. W. H., and Tolliday, J. D. *Ibid.*, **42**, 342 (1958).
17. Gustavson, K. H. *The Chemistry of Tanning Processes*, (New York: Academic Press, 1956) Chap. 9.
18. Moss, J. A. In preparation.
19. Bowes, J. H., and Moss, J. A. *J. Soc. Leather Trades Chemists*, **44**, 419 (1960).